SUPPORTING INFORMATION

1. Synthetic Procedures

Dichloromethane and 1,2-dichloroethane were washed twice with water, dried with $CaCl_2$ and distilled from CaH_2. Methanol was distilled from magnesium. CH_2Cl_2 and $ClCH_2CH_2Cl$ were stored over 4 Å molecular sieves and MeOH over 3Å molecular sieves. Melting points were determined on a Büchi apparatus and were uncorrected. Thin layer chromatography was performed on aluminium sheets coated with Silica gel 60 F_{254} (E. Merck). Compounds were visualized by spraying the TLC plates with dilute 15% aq H_2SO_4, followed by charring at 150°C for a few min. Column chromatography was performed on Silica-gel Geduran Si 60 (Merck). Optical rotations were recorded on a Perkin Elmer 241 polarimeter in a 1 cm cell at 21 °C. UV spectra were recorded in absolute ethanol on a UV-160A Shimadzu spectrophotometer ($c = 2.10^{-6}$ mol/L). ^{1}H and ^{13}C NMR spectra were recorded with a Bruker AC-200 spectrometer working at 200 MHz and 50 MHz respectively with Me_4Si as internal standard. Prime signals (') refer to the carbons of the phenyl group close to the sugar unit and double prime signals ('') refer to the second phenyl nucleus. Carbon chemical shift assignments are tentative. Elemental analyses were performed by the "Laboratoire Central d'Analyses du CNRS" (Vernaison, France).

4-Aminophenyl 2,3,4,6-tetra-O-acetyl-β-D-glucopyranoside (**1a**)

Compound **1a** was obtained in 44% yield from 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl bromide as described in the literature.[26,27] Product **1a** was an oil; *Rf* 0.23 (1:1 EtOAc-petroleum ether); $[\alpha]_D$ -18 (*c* 1.0, $CHCl_3$, lit.[25] -15.5). ^{1}H NMR ($CDCl_3$): δ 6.84 and 6.60 (2d, 4 H, *J* 8.7 Hz, C_6H_4), 5.22 (m, 3 H, H-2, H-3, H-4), 4.91 (d, 1 H, $J_{1,2}$ 7.3 Hz, H-1), 4.30 (dd, 1 H, $J_{5,6a}$ 5.1, $J_{6a,6b}$

12.3 Hz, H-6a), 4.16 (d, 1 H, $J_{5,6b}$ 2.5 Hz, H-6b), 3.79 (ddd, 1 H, $J_{4,5}$ 9.3 Hz, H-5), 3.55 (m, 2 H, NH_2), 2.09, 2.08, 2.04, 2.03 (4s, 12 H, 4 CH_3CO). ^{13}C NMR ($CDCl_3$): δ 170.64, 170.28, 169.45, 169.37 (4 CH_3CO), 149.79, 142.74, 119.01, 115.87 (C_6H_4), 101.65 (C-1), 72.84 (C-5), 71.89 (C-3), 71.32 (C-2), 68.42 (C-4), 62.00 (C-6), 20.72, 20.68, 20.63, 20.61 (4 CH$_3$CO).

4-Aminophenyl 2,3,4,6-tetra-O-acetyl-β-D-galactopyranoside (**1b**)

Compound **1b** was obtained in 60% yield from 2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl bromide as described in the literature.[26,27] Product **1b** was an oil; Rf 0.23 (1:1 EtOAc-petroleum ether); $[\alpha]_D$ 3.8 (*c* 1.0, $CHCl_3$, lit.[26] 5.83). ^{1}H NMR ($CDCl_3$): δ 6.84 and 6.62 (2d, 4 H, *J* 8.8 Hz, C_6H_4), 5.44 (dd, 1 H, $J_{1,2}$ 7.9, $J_{2,3}$ 10.5 Hz, H-2), 5.43 (bd, 1 H, $J_{3,4}$ 3.4, $J_{4,5}$ 0.5 Hz, H-4), 5.08 (dd, 1 H, H-3), 4.88 (d, 1 H, H-1), 4.28 (dd, 1 H, $J_{5,6a}$ 7.1, $J_{6a,6b}$ 11.3 Hz, H-6a), 4.15 (d, 1 H, $J_{5,6b}$ 6.3 Hz, H-6b), 4.00 (bdd, 1 H, H-5), 3.55 (m, 2 H, NH_2), 2.18, 2.09, 2.06, 2.01 (4s, 12 H, 4 CH_3CO). ^{13}C NMR ($CDCl_3$): δ 170.42, 170.34, 170.20, 169.47 (4 CH_3CO), 149.98, 142.59, 118.90, 115.92 (C_6H_4), 101.16 (C-1), 70.96, 70.88 (C-3, C-5), 68.87 (C-2), 67.00 (C-4), 61.37 (C-6), 20.80, 20.69, 20.69, 20.63 (4 CH$_3$CO).

4-Aminophenyl 4-O-(2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyl)-2,3,6-tri-O-acetyl-β-D-glucopyranoside (**1c**)

Compound **1c** was obtained in 40% yield from 4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-2,3,6-tri-*O*-acetyl-α-D-glucopyranosyl bromide as described in the literature.[26,27] Product **1c** was an oil; Rf 0.35 (3:1 EtOAc-petroleum ether); $[\alpha]_D$ -12.6 (*c* 1.0, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 6.82 and 6.60 (2d, 4 H, *J* 8.7 Hz, C_6H_4), 5.36 (bd, 1 H, $J_{3,4}$ 3.3, $J_{4,5}$

0.5 Hz, H-4_{Gal}), 5.26 (dd, 1 H, $J_{2,3}$ 10.2, $J_{3,4}$ 10.2 Hz, H-3_{Glc}), 5.21 (m, 2 H, H-2_{Glc}, H-2_{Gal}), 4.97 (dd, 1 H, $J_{2,3}$ 10.4 Hz, H-3_{Gal}), 4.87 (d, 1 H, $J_{1,2}$ 7.6 Hz, H-1_{Glc}), 4.51 (d, 1 H, $J_{1,2}$ 7.8 Hz, H-1_{Gal}), 4.49 (m, 1 H, H-$6a_{Glc}$), 4.04 (m, 3 H, H-$6b_{Glc}$, H-$6a_{Gal}$, H-$6b_{Gal}$), 3.89 (bdd, 1 H, $J_{5,6a}$ 6.5, $J_{5,6b}$ 6.5 Hz, H-5_{Gal}), 3.87 (dd, 1 H, $J_{3,4}$ 8.3 Hz, H-4_{Glc}) 3.71 (m, 1 H, H-5_{Glc}), 3.52 (m, 2 H, NH_2), 2.16, 2.11, 2.07, 2.07, 2.06, 2.05, 1.97 (7s, 21 H, 7 CH_3CO). ^{13}C NMR ($CDCl_3$): δ 170.35, 170.35, 170.16, 170.05, 169.79, 169.64, 169.12 (7 CH_3CO), 149.67, 142.76, 118.91, 115.79 (C_6H_4), 101.04 (C-1_{Glc}), 100.30 (C-1_{Gal}), 76.30 (C-4_{Glc}), 72.87, 72.68 (C-5_{Glc}, C-5_{Gal}), 71.60, 70.96, 70.69 (C-2_{Glc}, C-3_{Glc}, C-3_{Gal}), 69.12 (C-2_{Gal}), 66.70 (C-4_{Gal}), 62.07 (C-6_{Glc}), 60.90 (C-6_{Gal}), 20.79, 20.79, 20.69, 20.69, 20.69, 20.61, 20.50 (7 CH_3CO).

4-Aminophenyl 2,3,4-tri-O-acetyl-β-D-xylopyranoside (**1d**)

Compound **1d** was obtained in 57% yield from 2,3,4-tri-*O*-acetyl-α-D-xylopyranosyl bromide as described in the literature.[26,27] Product **1d** was a solid; mp 146-148 °C (lit.[28] mp 154-155 °C); R_f 0.20 (1:2 EtOAc-petroleum ether); $[\alpha]_D$ -40.0 (*c* 1.1, $CHCl_3$, lit.[28] -41.9). ^{1}H NMR ($CDCl_3$): δ 6.83 and 6.61 (2d, 4 H, *J* 8.8 Hz, C_6H_4), 5.23 (dd, 1 H, $J_{2,3}$ 7.9, $J_{3.4}$ 7.9 Hz, H-3), 5.14 (dd, 1 H, $J_{1,2}$ 6.1 Hz, H-2), 5.01 (ddd, 1 H, $J_{4,5a}$ 4.9, $J_{4,5b}$ 8.2 Hz, H-4), 4.97 (d, 1 H, H-1), 4.20 (dd, 1 H, $J_{5a,5b}$ 11.9 Hz, H-5a), 3.54 (m, 2 H, NH_2), 3.47 (dd, 1 H, H-5b), 2.09, 2.07, 2.07 (3s, 9 H, 3 CH_3CO). ^{13}C NMR ($CDCl_3$): δ 170.07, 169.87, 169.45 (3 CH_3CO), 149.51, 142.55, 118.83, 115.97 (C_6H_4), 100.23 (C-1), 71.22, 70.68 (C-2, C-3), 68.73 (C-4), 62.05 (C-5), 20.74, 20.74, 20.74 (3 CH_3CO).

4-Aminophenyl 2,3,4,6-tri-O-acetyl-α-D-mannopyranoside (**1e**)

Compound **1e** was obtained in 35% yield from 1,2,3,4,6-penta-*O*-acetyl-β-D-mannopyranose as described in the literature.[30,27] Product **1e** was an oil; R_f 0.48 (3:2 EtOAc-petroleum ether); $[\alpha]_D$ 69.3 (*c* 1.0, $CHCl_3$, lit.[29] 71.2). ^{1}H NMR ($CDCl_3$): δ 6.90 and 6.62 (2d, 4 H, *J* 8.8 Hz, C_6H_4), 5.55 (dd, 1 H, $J_{2,3}$ 3.4, $J_{3,4}$ 10.0 Hz, H-3), 5.43 (dd, 1 H, $J_{1,2}$ 1.8 Hz, H-2), 5.36 (d, 1 H, H-1), 5.35 (dd, 1 H, $J_{4,5}$ 9.8 Hz, H-4), 4.29 (dd, 1 H, $J_{5,6a}$ 5.1, $J_{6a,6b}$ 12.2 Hz, H-6a), 4.16 (ddd, 1 H, $J_{5,6b}$ 2.1 Hz, H-5), 4.09 (dd, 1 H, H-6b), 2.18, 2.06, 2.06, 2.03 (4s, 12 H, 4 CH_3CO).

General Procedure for the Preparation of Diazonium Tetrafluoroborates

Boron trifluoride etherate (0.190 mL, 1.5 mmol) and a solution of 4-aminophenyl glycoside **1a**-**e** (1.0 mmol) in CH_2Cl_2 (2 mL) were successively added in a 50 mL three-necked flask, cooled to –15 °C in an ice-salt mixture. A solution of *t*-butyl nitrite (0.144 mL, 1.2 mmol) in CH_2Cl_2 (1.2 mL) was then added dropwise over 15 min and the mixture was stirred for 20 min at –15 °C, then for 30 min at 0 °C. Addition of *n*-pentane (10 mL) caused precipitation of the product. The supernatant phase was removed; the product was then dissolved in CH_2Cl_2 (3 mL) and precipitated by addition of *n*-pentane as already described. The precipitation process was repeated, and finally the brown product was concentrated twice from a $CHCl_3$/*n*-hexane mixture and used directly without purification in the next step.

4-(2,3,4,6-Tetra-O-acetyl-β-D-glucopyranosyloxy)phenyldiazonium tetrafluoroborate (**2a**)

Compound **2a** was obtained from **1a** in quantitative yield as described above. Product **2a** was a brown oil; $[\alpha]_D$ -2.0 (*c* 0.5, CH_3COCH_3). ^{1}H NMR (CD_3COCD_3): δ 8.84 (d, 2 H, *J* 9.4 Hz, H-2', H-6'), 7.69 (d, 2 H, *J* 9.4 Hz, H-3', H-5'), 5.93 (d, 1 H, $J_{1,2}$ 7.6 Hz, H-1), 5.45 (dd, 1 H, $J_{2.3}$ 9.5, $J_{3,4}$ 9.2 Hz, H-3), 5.32 (dd, 1 H, H-2), 5.21 (d, 1 H, $J_{4,5}$ 9.6 Hz, H-4), 4.40 (ddd, 1 H, $J_{5,6a}$ 4.6, $J_{5,6b}$ 2.1

Hz, H-5), 4.32 (dd, 1 H, $J_{6a,6b}$ 12.1 Hz, H-6a), 4.22 (dd, 1 H, H-6b), 2.08, 2.08, 2.01, 1.99 (4s, 12 H, 4 CH_3CO). ^{13}C NMR ($CDCl_3$): δ 170.31, 170.26, 169.70, 169.70 (4 CH_3*C*O), 165.87 (C-4'), 135.78 (C-2', C-6'), 119.38 (C-3', C-5'), 105.18 (C-1'), 97.08 (C-1), 72.40, 72.14 (C-3, C-5), 70.70 (C-2), 67.61 (C-4), 61.46 (C-6), 20.53, 20.53, 20.53, 20.53 (4 *C*H_3CO).

4-(2,3,4,6-Tetra-O-acetyl-β-D-galactopyranosyloxy)phenyldiazonium tetrafluoroborate (**2b**)

Compound **2b** was obtained from **1b** in quantitative yield as described above. Product **2b** was a brown oil; $[\alpha]_D$ -7.5 (*c* 1.0, $CHCl_3$). ^{1}H NMR (CD_3COCD_3): δ 8.85 (d, 2 H, *J* 9.4 Hz, H-2', H-6'), 7.69 (d, 2 H, *J* 9.4 Hz, H-3', H-5'), 5.91 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1), 5.53 (dd, 1 H, $J_{3,4}$ 3.4, $J_{4,5}$ 1.0 Hz, H-4), 5.51 (dd, 1 H, $J_{2.3}$ 10.4 Hz, H-2), 5.32 (dd, 1 H, H-3), 4.63 (ddd, 1 H, $J_{5,6a}$ 6.3, $J_{5,6b}$ 6.3 Hz, H-5), 4.21 (m, 2 H, H-6a, H-6b), 2.18, 2.05, 2.01, 1.97 (4s, 12 H, 4 CH_3CO). ^{13}C NMR (CD_3COCD_3): δ 171.33, 171.26, 170.85, 170.52 (4 CH_3*C*O), 167.50 (C-4'), 137.64 (C-2', C-6'), 120.73 (C-3', C-5'), 107.64 (C-1'), 99.15 (C-1), 73.18, 71.84 (C-3, C-5), 69.48 (C-2), 68.60 (C-4), 62.60 (C-6), 21.22, 21.18, 21.15, 20.10 (4 *C*H_3CO); HRMS Calcd for $C_{20}H_{23}N_2O_{10}$ (451.1353). Found: 451.1350.

*4-[4-*O*-(2,3,4,6-Tetra-O-acetyl-β-D-galactopyranosyl)-2,3,6-tri-O-acetyl-β-D-glucopyranosyloxy]phenyldiazonium tetrafluoroborate* (**2c**)

Compound **2c** was obtained from **1c** in quantitative yield as described above. Product **2c** was a brown oil; $[\alpha]_D$ -33.4 (*c* 1.0, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 8.52 (d, 2 H, *J* 8.7 Hz, H-2', H-6'), 7.37 (d, 2 H, *J* 8.7 Hz, H-3', H-5'), 5.49 (dd, 1 H, $J_{1,2}$ 6.6 Hz, H-1_{Glc}), 5.36 (bd, 1 H, $J_{3,4}$ 3.1, $J_{4,5}$ 0.5 Hz, H-4_{Gal}), 5.31-5.20 (m, 2 H, H-2_{Glc}, H-3_{Glc}), 5.09 (dd, 1 H, $J_{1,2}$ 7.5, $J_{2,3}$ 10.3 Hz, H-2_{Gal}), 4.98 (dd, 1

H, H-3_{Gal}), 4.63 (m, 1 H, H-$6a_{Glc}$), 4.53 (d, 1 H, H-1_{Gal}), 4.13-3.92 (m, 6 H, H-4_{Glc}, H-5_{Glc}, H-5_{Gal}, H-$6b_{Glc}$, H-$6a_{Gal}$, H-$6b_{Gal}$), 2.15, 2.07, 2.07, 2.07, 2.05, 2.05, 1.97 (7s, 21 H, 7 CH_3CO).

4-(2,3,4-Tri-O-acetyl-β-D-xylopyranosyloxy)phenyldiazonium tetrafluoroborate (**2d**)

Compound **2d** was obtained from **1d** in quantitative yield as described above. Product **2d** was a brown oil); $[\alpha]_D$ -39 (*c* 0.2, CH_3COCH_3). ^{1}H NMR (CD_3COCD_3): δ 8.83 (d, 2 H, *J* 9.3 Hz, H-2', H-6'), 7.67 (d, 2 H, *J* 9.3 Hz, H-3', H-5'), 5.90 (d, 1 H, $J_{1,2}$ 5.5 Hz, H-1), 5.32 (dd, 1 H, $J_{2,3}$ 8.9, $J_{3,4}$ 8.0 Hz, H-3), 5.25 (dd, 1 H, H-2), 5.04 (ddd, 1 H, $J_{4,5a}$ 4.6, $J_{4,5b}$ 7.7 Hz, H-4), 4.25 (dd, 1 H, $J_{5a,5b}$ 12.1 Hz, H-5a), 4.21 (d, 1 H, H-5b), 2.06, 2.05, 2.05 (3s, 9 H, 3 CH_3CO). ^{13}C NMR (CD_3COCD_3): δ 170.66, 170.48, 170.17 (3 CH_3*C*O), 167.24 (C-4'), 137.41 (C-2', C-6'), 120.49 (C-3', C-5'), 107.13 (C-1'), 98.68 (C-1), 71.09, 70.45 (C-2, C-3), 69.05 (C-4), 63.19 (C-5), 20.99, 20.96, 20.89 (3 *C*H_3CO).

4-(2,3,4,6-Tetra-O-acetyl-α-D-mannopyranosyloxy)phenyldiazonium tetrafluoroborate (**2e**)

Compound **2e** was obtained from **1e** in quantitative yield as described above. Product **2e** was a brown oil; $[\alpha]_D$ 103.2 (*c* 0.5, CH_3COCH_3). ^{1}H NMR (CD_3COCD_3): δ 8.89 (d, 2 H, *J* 9.4 Hz, H-2', H-6'), 7.80 (d, 2 H, *J* 9.4 Hz, H-3', H-5'), 6.15 (d, 1 H, $J_{1,2}$ 1.2 Hz, H-1), 5.56 (d, 1 H, $J_{2,3}$ 3.5 Hz, H-2), 5.50 (dd, 1 H, $J_{3,4}$ 9.3 Hz, H-3), 5.37 (d, 1 H, $J_{4,5}$ 9.9 Hz, H-4), 4.25 (dd, 1 H, $J_{5,6a}$ 5.4, $J_{6a,6b}$ 11.4 Hz, H-6a), 4.19 (ddd, 1 H, $J_{5,6b}$ 2.1 Hz, H-5), 4.05 (dd, 1 H, H-6b), 2.18, 2.05, 1.97, 1.96 (4s, 12 H, 4 CH_3CO). ^{13}C NMR (CD_3COCD_3): δ 171.01, 170.70, 170.57, 170.53 (4 CH_3*C*O), 166.55 (C-4'), 137.29 (C-2', C-6'), 120.82 (C-3', C-5'), 107.34 (C-1'), 97.53 (C-1), 71.63 (C-2), 69.70, 69.31 (C-3, C-5), 66.41 (C-4), 62.96 (C-6), 20.95, 20.95, 20.95, 20.95 (4 *C*H_3CO).

General Procedure for the Diazo Coupling

Dialkylamine (1.1 mmol), water (5 mL), sodium carbonate (0.159 g, 1.50 mmol), a solution of the diazonium salt (**2a**-**e**) (1.0 mmol) in 1,2-dichloroethane (4 mL) and picric acid (30 mg) were successively added in a 50 mL flask and the mixture was stirred at room temperature for 6h. After dilution with CH_2Cl_2 (20 mL), the organic phase was separated and washed with water (2x5 mL), dried and concentrated. The crude azo compound **4a-e** was purified by column chromatography.

4-(4'-N,N-Diethylaminophenylazo)phenyl 2,3,4,6-tetra-O-acetyl-β-D-glucopyranoside (**3a**)

Compound **3a** was obtained from **2a** and *N*,*N*-diethylaniline[35] in 43% yield as described above, after purification by column chromatography (1:2 EtOAc-petroleum ether). Product **3a** was a red amorphous solid : R_f 0.43 (1:2 EtOAc-petroleum ether); $[\alpha]_D$ 35.4 (*c* 1.0, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 7.83-7.81 (m, 4 H, H-3', H-5', H-2'', H-6''), 7.07 (d, 2 H, *J* 8.9 Hz, H-2', H-6'), 6.72 (d, 2 H, *J* 9.1 Hz, H-3'', H-5''), 5.33 (d, 1 H, $J_{1,2}$ 8.1 Hz, H-1), 5.32-5.14 (m, 3 H, H-2, H-3, H-4), 4.33 (d, 1 H, $J_{5,6a}$ 5.4, $J_{6a,6b}$ 12.3 Hz, H-6a), 4.19 (dd, 1 H, $J_{5,6b}$ 2.3 Hz, H-6b), 3.91 (ddd, 1 H, $J_{4,5}$ 9.7 Hz, H-5), 3.47 (q, 4 H, *J* 7.0 Hz, N(CH_2R)$_2$), 2.10, 2.09, 2.07, 2.06 (4s, 12 H, 4 CH_3CO), 1.23 (t, 6 H, 2 CH_3). ^{13}C NMR ($CDCl_3$): δ 170.62, 170.25, 169.46, 169.35 (4 CH_3*C*O), 157.57 (C-1'), 150.06 (C-4''), 149.36 (C-4'), 143.05 (C-1''), 125.17 (C-2'', C-6''), 123.59 (C-3', C-5'), 117.16 (C-2', C-6'), 110.05 (C-3'', C-5''), 99.06 (C-1), 72.78, 72.17 (C-3, C-5), 71.24 (C-2), 68.36 (C-4), 62.02 (C-6), 44.73 (N(*C*H$_2$R)$_2$), 20.75, 20.65, 20.65, 20.65 (4 *C*H$_3$CO), 12.70 (2 *C*H$_3$). Anal. Calcd for $C_{30}H_{37}N_3O_{10}$ (599.62): C, 60.09; H, 6.22; N, 7.01. Found; C, 60.02; H, 6.16; N, 6.65.

4-(4'-N,N-Didodecylaminophenylazo)phenyl 2,3,4,6-tetra-O-acetyl-β-D-glucopyranoside (**4a**)

Compound **4a** was obtained from **2a** and *N*,*N*-didodecylaniline[37] in 63% yield as described above, after purification by column chromatography (1:2 EtOAc-petroleum ether). Product **4a** was a red amorphous solid: R_f 0.70 (1:2 EtOAc-petroleum ether); $[\alpha]_D$ 23.1 (*c* 1.0, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 7.82-7.80 (m, 4 H, H-3', H-5', H-2'', H-6''), 7.07 (d, 2 H, *J* 9.0 Hz, H-2', H-6'), 6.68 (d, 2 H, *J* 9.1 Hz, H-3'', H-5''), 5.33 (d, 1 H, $J_{1,2}$ 8.0 Hz, H-1), 5.32-5.14 (m, 3 H, H-2, H-3, H-4), 4.33 (d, 1 H, $J_{5,6a}$ 5.2, $J_{6a,6b}$ 12.1 Hz, H-6a), 4.19 (dd, 1 H, $J_{5,6b}$ 2.1 Hz, H-6b), 3.91 (ddd, 1 H, $J_{4,5}$ 9.7 Hz, H-5), 3.35 (q, 4 H, *J* 7.0 Hz, N(CH_2R)$_2$), 2.10, 2.09, 2.07, 2.06 (4s, 12 H, 4 CH_3CO), 1.59 (m, 4 H, N(CH$_2$CH_2R)$_2$), 1.28 (m, 36 H, 18 CH_2), 0.88 (t, 6H, J 6.6 Hz, 2 CH_3). ^{13}C NMR ($CDCl_3$): δ 170.58, 170.22, 169.43, 169.32 (4 CH_3*C*O), 157.56 (C-1'), 150.45 (C-4''), 149.39 (C-4'), 142.99 (C-1''), 125.10 (C-2'', C-6''), 123.60 (C-3', C-5'), 117.16 (C-2', C-6'), 111.12 (C-3'', C-5''), 99.05 (C-1), 72.80, 72.17 (C-3, C-5), 71.25 (C-2), 68.36 (C-4), 62.02 (C-6), 51.27 (N(*C*H$_2$R)$_2$), 31.96, 29.68, 29.54, 29.39, 27.39, 27.15, 22.77 (*C*H$_2$ alkyl chains), 20.73, 20.66, 20.66, 20.66 (4 *C*H$_3$CO), 14.17 (2 *C*H$_3$). Anal. Calcd for $C_{50}H_{77}N_3O_{10}$ (880.19): C.68.23; H, 8.82; N, 4.77. Found; C.68.19; H, 8.82; N, 4.77.

4-(4'-N,N-Didodecylaminophenylazo)phenyl 2,3,4,6-tetra-O-acetyl-β-D-galactopyranoside (**4b**)

Compound **4b** was obtained from **2b** and *N*,*N*-didodecylaniline[37] in 60% yield as described above, after purification by column chromatography (1:3 EtOAc-petroleum ether). Product **4b** was a red amorphous solid: R_f 0.44 (1:3 EtOAc-petroleum ether); $[\alpha]_D$ 49.4 (*c* 1.0, $CHCl_3$). ^{1}H

NMR ($CDCl_3$): δ 7.84-7.78 (m, 4 H, H-3', H-5', H-2'', H-6''), 7.08 (d, 2 H, *J* 8.9 Hz, H-2', H-6'), 6.68 (d, 2 H, *J* 9.1 Hz, H-3'', H-5''), 5.54 (dd, 1 H, $J_{1,2}$ 8.0, $J_{2,3}$ 10.3 Hz, H-2), 5.49 (m, 1 H, H-4), 5.14 (dd, 1 H, $J_{3,4}$ 3.4 Hz, H-3), 5.12 (d, 1 H, H-1), 4.31-4.21 (m, 2 H, H-6a, H-6b), 4.11 (bdd, 1 H, $J_{4,5}$ 0.6, $J_{5,6a}$ 6.5, $J_{5,6b}$ 6.5 Hz, H-5), 3.36 (m, 4 H, $N(CH_2R)_2$), 2.20, 2.09, 2.09, 2.03 (4s, 12 H, 4 CH_3CO), 1.61 (m, 4 H, $N(CH_2CH_2R)_2$), 1.27 (m, 36 H, 18 CH_2), 0.89 (t, 6H, J 6.2 Hz, 2 CH_3). ^{13}C NMR ($CDCl_3$): δ 170.38, 170.27, 170.11, 169.42 (4 CH_3CO), 157.63 (C-1'), 150.43 (C-4''), 149.34 (C-4'), 142.98 (C-1''), 125.08 (C-2'', C-6''), 123.58 (C-3', C-5'), 117.09 (C-2', C-6'), 111.10 (C-3'', C-5''), 99.56 (C-1), 71.18, 70.89 (C-3, C-5), 68.71 (C-2), 66.98 (C-4), 61.49 (C-6), 51.26 ($N(CH_2R)_2$), 31.96, 29.68, 29.54, 29.39, 27.39, 27.15, 22.74 (CH_2 alkyl chains), 20.78, 20.70, 20.70, 20.62 (4 CH_3CO), 14.17 (2 CH_3). Anal. Calcd for $C_{50}H_{77}N_3O_{10}$ (880.19): C, 68.23; H, 8.82; N, 4.77. Found; C, 68.16; H, 8.74; N, 4.76.

4-(4'-N,N-Didodecylaminophenylazo)phenyl 4-O-(2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyl)-2,3,6-tri-O-acetyl-β-D-glucopyranoside (**4c**)

Compound **4c** was obtained from **2c** and *N*,*N*-didodecylaniline[37] in 72% yield as described above, after purification by column chromatography (2:3 EtOAc-petroleum ether). Product **4c** was a red amorphous solid: R_f 0.47 (2:3 EtOAc-petroleum ether); $[\alpha]_D$ 13.6 (*c* 1.0, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 7.83-7.77 (m, 4 H, H-3', H-5', H-2'', H-6''), 7.05 (d, 2 H, *J* 8.9 Hz, H-2', H-6'), 6.67 (d, 2 H, *J* 9.1 Hz, H-3'', H-5''), 5.37 (dd, 1 H, $J_{3,4}$ 3.4, $J_{4,5}$ 0.6 Hz, H-4_{Gal}), 5.31-5.17 (m, 3 H, H-2_{Glc}, H-3_{Glc}, H-2_{Gal}), 5.13 (dd, 1 H, $J_{1,2}$ 7.6 Hz, H-1_{Glc}), 4.97 (dd, 1 H, $J_{2,3}$ 10.4, $J_{3,4}$ 3.4 Hz, H-3_{Gal}), 4.53 (dd, 1 H, $J_{1,2}$ 7.8 Hz, H-1_{Gal}), 4.51 (d, 1 H, H-$6a_{Glc}$), 4.22-4.11 (m, 3 H, H-$6b_{Glc}$, H-$6a_{Gal}$, H-$6b_{Gal}$), 3.97-3.85 (m, 3 H, H-4_{Glc}, H-5_{Glc}, H-5_{Gal}), 3.35 (m, 4 H, $N(CH_2R)_2$), 2.17, 2.10, 2.09,

2.09, 2.08, 2.08, 1.98 (7s, 21 H, 7 CH_3CO), 1.64 (m, 4 H, N($CH_2CH_2R)_2$), 1.27 (m, 36 H, 18 CH_2), 0.89 (t, 6H, J 6.2 Hz, 2 CH_3). ^{13}C NMR ($CDCl_3$): δ 170.36, 170.36, 170.16, 170.05, 169.75, 169.62, 169.13 (7 CH_3CO), 157.53 (C-1'), 150.43 (C-4''), 149.31 (C-4'), 142.95 (C-1''), 125.07 (C-2'', C-6''), 123.55 (C-3', C-5'), 117.09 (C-2', C-6'), 111.10 (C-3'', C-5''), 101.16 (C-1_{Gal}), 98.66 (C-1_{Glc}), 76.34 (C-4_{Glc}), 72.91, 71.55, 71.01, 70.80 (C-2_{Glc}, C-3_{Glc}, C-5_{Glc}, C-3_{Gal}, C-5_{Gal}), 69.15 (C-2_{Gal}), 66.72 (C-4_{Gal}), 62.17 (C-6_{Glc}), 60.93 (C-6_{Gal}) 51.26 (N($CH_2R)_2$), 31.95, 29.66, 29.52, 29.38, 27.38, 27.14, 22.72 (CH_2 alkyl chains), 20.83, 20.80, 20.80, 20.67, 20.67, 20.67, 20.54 (7 CH_3CO), 14.16 (2 CH_3). Anal. Calcd for $C_{62}H_{93}N_3O_{18}$ (1168.41): C, 63.73; H, 8.03; N, 3.62. Found; C, 63.73; H, 8.02; N, 3.60.

4-(4'-N,N-Didodecylaminophenylazo)phenyl 2,3,4-tri-O-acetyl-β-D-xylopyranoside (**4d**)

Compound **4d** was obtained from **2d** and *N*,*N*-didodecylaniline[37] in 55% yield as described above, after purification by column chromatography (2:5 EtOAc-petroleum ether). Product **4d** was a red amorphous solid: R_f 0.60 (2:5 EtOAc-petroleum ether); $[\alpha]_D$ -12.5 (*c* 1.0, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 7.84-7.79 (m, 4 H, H-3', H-5', H-2'', H-6''), 7.08 (d, 2 H, *J* 8.9 Hz, H-2', H-6'), 6.68 (d, 2 H, *J* 9.2 Hz, H-3'', H-5''), 5.31-5.17 (m, 3 H, H-1, H-2, H-3), 5.05 (ddd, 1 H, $J_{3,4}$ 6.9, $J_{4,5a}$ 4.6, $J_{4,5b}$ 7.5 Hz, H-4), 4.26 (dd, 1 H, $J_{5a,5b}$ 12.2 Hz, H-5a), 3.58 (dd, 1 H, H-5b), 3.35 (m, 4 H, N($CH_2R)_2$), 2.11, 2.10, 2.10 (3s, 9 H, 3 CH_3CO), 1.62 (m, 4 H, N($CH_2CH_2R)_2$), 1.28 (m, 36 H, 18 CH_2), 0.89 (t, 6 H, *J* 6.6 Hz, 2 CH_3). ^{13}C NMR ($CDCl_3$): δ 169.95, 169.85, 169.41 (3 CH_3CO), 157.33 (C-1'), 150.40 (C-4''), 149.35 (C-4'), 143.01 (C-1''), 125.06 (C-2'', C-6''), 123.63 (C-3', C-5'), 117.03 (C-2', C-6'), 111.11 (C-3'', C-5''), 98.45 (C-1), 70.65, 70.11 (C-2, C-3), 68.50 (C-4), 61.91 (C-5), 51.27 (N($CH_2R)_2$), 31.98, 29.69, 29.55, 29.40, 27.40, 27.17 (CH_2 alkyl chains),

20.81, 20.81, 20.81 (3 *C*H_3CO), 14.18 (2 *C*H_3). Anal. Calcd for $C_{47}H_{73}N_3O_8$ (808.07): C, 69.85; H, 9.11; N, 5.20. Found; C, 69.32; H, 8.89; N, 5.19.

4-(4'-N,N-Didodecylaminophenylazo)phenyl 2,3,4,6-tetra-O-acetyl-α-D-mannopyranoside (**4e**)

Compound **4e** was obtained from **2e** and *N,N*-didodecylaniline[37] in 71% yield as described above, after purification by column chromatography (1:2 EtOAc-petroleum ether). Product **4e** was a red amorphous solid: R_f 0.60 (1:2 EtOAc-petroleum ether); $[\alpha]_D$ 61.5 (*c* 1.0, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 7.84-7.79 (m, 4 H, H-3', H-5', H-2'', H-6''), 7.18 (d, 2 H, *J* 9.0 Hz, H-2', H-6'), 6.68 (d, 2 H, *J* 9.2 Hz, H-3'', H-5''), 5.60 (d, 1 H, $J_{1,2}$ 1.7 Hz, H-1), 5.59 (dd, 1 H, $J_{2,3}$ 3.5, $J_{3,4}$ 10.0 Hz, H-3), 5.49 (dd, 1 H, H-2), 5.39 (dd, 1 H, $J_{4,5}$ 10.0 Hz, H-4), 4.35 (dd, 1 H, $J_{5,6a}$ 5.5, $J_{6a,6b}$ 12.2 Hz, H-6a), 4.11 (dd, 1 H, $J_{5,6b}$ 2.0 Hz, H-6b), 4.10 (m, 1 H, H-5), 3.35 (m, 4 H, N(CH_2R)$_2$), 2.22, 2.07, 2.05, 2.04 (4s, 12 H, 4 CH_3CO), 1.66 (m, 4 H, N(CH$_2$CH_2R)$_2$), 1.28 (m, 36 H, 18 CH_2), 0.89 (t, 6H, *J* 6.6 Hz, 2 CH_3). ^{13}C NMR ($CDCl_3$): δ 170.56, 169.96, 169.93, 169.78 (4 CH_3*C*O), 156.25 (C-1'), 150.43 (C-4''), 149.18 (C-4'), 143.01 (C-1''), 125.07 (C-2'', C-6''), 123.63 (C-3', C-5'), 116.76 (C-2', C-6'), 111.12 (C-3'', C-5''), 95.85 (C-1), 69.41, 69.35, 68.94 (C-2, C-3, C-5), 66.02 (C-4), 62.18 (C-6), 51.27 (N(*C*H$_2$R)$_2$), 31.96, 29.68, 29.54, 29.39, 27.40, 27.16, 22.73 (*C*H_2 alkyl chains), 20.90, 20.72, 20.72, 20.72 (4 *C*H_3CO), 14.16 (2 *C*H_3). Anal. Calcd for $C_{50}H_{77}N_3O_{10}$ (880.19): C, 68.23; H, 8.82; N, 4.77. Found; C, 67.95; H, 8.78; N, 4.79.

General Procedure for De-O-acetylation

Compounds **4a**-**e** (0.50 mmol) were treated overnight in methanol (50 mL) containing a catalytic amount of sodium. After neutralization of the solution with amberlyst IR 120 [H^+],

filtration and concentration, the product was purified on a short column of silica-gel using pure ethyl acetate or ethanol-ethyl acetate mixtures.

4-(4'-N,N-Didodecylaminophenylazo)phenyl β-D-glucopyranoside (**5a**)

Compound **5a** was obtained from **4a** in 91% yield as described above, after purification by column chromatography (8:1 EtOAc-EtOH). Product **5a** was a red amorphous solid; R_f 0.70 (8:1 EtOAc-EtOH); $[\alpha]_D$ -76.5 (*c* 1.0, $CHCl_3$). UV/vis: λ_{max} = 270 nm, ε = 114500; λ_{max} = 416 nm, ε = 21500. ^{1}H NMR (CD_3COCD_3): δ 7.81 (d, 4 H, *J* 8.9 Hz, H-3', H-5', H-2'', H-6''), 7.18 (d, 2 H, *J* 8.9 Hz, H-2', H-6'), 6.80 (d, 2 H, *J* 8.9 Hz, H-3'', H-5''), 5.07 (d, 1 H, $J_{1,2}$ 7.1 Hz, H-1), 3.92 (d, 1 H, $J_{5,6a}$ 1.8, $J_{6a,6b}$ 11.5 Hz, H-6a), 3.74 (d, 1 H, $J_{5,6b}$ 1.8, Hz, H-6b), 3.61-3.41 (m, 11 H, H-2, H-3, H-4, H-5, 3 O*H*, N(CH_2R)$_2$), 1.67 (m, 4 H, N(CH_2CH_2R)$_2$), 1.30 (m, 36 H, 18 CH_2), 0.88 (t, 6H, *J* 6.6 Hz, 2 CH_3). ^{13}C NMR ($CDCl_3$): δ 158.27 (C-1'), 150.47 (C-4''), 149.18 (C-4'), 143.43 (C-1''), 125.47 (C-2'', C-6''), 124.18 (C-3', C-5'), 117.32 (C-2', C-6'), 111.41 (C-3'', C-5''), 100.91 (C-1), 76.42,76.31 (C-3, C-5), 73.72 (C-2), 69.76 (C-4), 61.48 (C-6), 51.56 (N(*C*H_2R)$_2$), 32.35, 31.12, 30.08, 29.95, 29.79, 27.79, 27.58, 213.11 (*C*H_2 alkyl chains), 14.54 (2 *C*H_3). Anal. Calcd for $C_{42}H_{69}N_3O_6$,0.5H_2O (721.00): C, 69.96; H, 9.78; N, 5.83. Found; C, 69.75; H, 9.79; N, 5.95.

4-(4'-N,N-Didodecylaminophenylazo)phenyl β-D-galactopyranoside (**5b**)

Compound **5b** was obtained from **4b** in 93% yield as described above. Product **5b** was a red amorphous solid : R_f 0.70 (8:1 EtOAc-EtOH); $[\alpha]_D$ –122.0 (*c* 1.0, $CHCl_3$). UV/vis: λ_{max} = 270 nm, ε = 169500; λ_{max} = 414 nm, ε = 18500. ^{1}H NMR ($CDCl_3$): δ 7.76 (d, 4 H, *J* 8.8 Hz, H-3', H-5', H-2'', H-6''), 7.19 (d, 2 H, *J* 8.8 Hz, H-2', H-6'), 6.65 (d, 2 H, *J* 8.8 Hz, H-3'', H-5''), 4.93 (d, 1

H, $J_{1,2}$ 7.7 Hz, H-1), 3.92 (bd, 1 H, $J_{3,4}$ 9.7, $J_{4,5}$ 0.5 Hz, H-4), 3.84 (dd, 1 H, $J_{2,3}$ 9.7 Hz, H-2), 3.81-3.67 (m, 3 H, H-5, H-6a, H-6b), 3.60 (dd, 1 H, H-3), 3.31 (m, 4 H, N(CH_2R)$_2$), 1.55 (m, 4 H, N(CH$_2$CH_2R)$_2$), 1.28 (m, 36 H, 18 CH_2), 0.90 (t, 6H, *J* 6.6 Hz, 2 CH_3). ^{13}C NMR ($CDCl_3$): δ 158.06 (C-1'), 150.22 (C-4''), 148.84 (C-4'), 143.11 (C-1''), 125.18 (C-2'', C-6''), 123.85 (C-3', C-5'), 117.09 (C-2', C-6'), 111.14 (C-3'', C-5''), 100.06 (C-1), 74.58, 73.59 (C-3, C-5), 71.12 (C-2), 69.05 (C-4), 61.52 (C-6), 51.26 (N(*C*H$_2$R)$_2$), 32.00, 29.78, 29.73, 29.60, 29.44, 27.48, 27.24, 22.76 (*C*H$_2$ alkyl chains), 14.17 (2 *C*H$_3$). Anal. Calcd for $C_{42}H_{69}N_3O_6$,0.5H_2O (721.00): C, 69.96; H, 9.78; N, 5.83. Found; C, 69.74; H, 9.73; N, 5.78. HRMS Calcd for $C_{42}H_{68}N_3O_6$ $[M-H]^+$ (710.5108). Found: 710.5113.

4-(4'-N,N-Didodecylaminophenylazo)phenyl 4-*O*-*β*-*D*-*galactopyranosyl*-*β*-*D*-*glucopyranoside* (**5c**)

Compound **5c** was obtained from **4c** in 92% yield as described above after purification by column chromatography (2:1 EtOAc-EtOH). Product **5c** was a red amorphous solid: R_f 0.70 (2:1 EtOAc-EtOH); $[\alpha]_D$ 31.6 (*c* 0.5, $CHCl_3$). UV/vis: λ_{max} = 271 nm, ε = 179000; λ_{max} = 412 nm, ε = 14500. ^{1}H NMR (C_5D_5N+D_2O): δ 8.23 (d, 2 H, *J* 8.1 Hz, H-3', H-5'), 8.09 (d, 2 H, *J* 8.4 Hz, H-2'', H-6''), 7.45 (d, 2 H, H-2', H-6'), 6.98 (d, 2 H, H-3'', H-5''), 5.63 (d, 1 H, $J_{1,2}$ 7.2 Hz, H-1$_{Glc}$), 5.13 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1$_{Gal}$), 4.57-4.15 (m, 12 H, H-2$_{Glc}$, H-3$_{Glc}$, H-4$_{Glc}$, H-5$_{Glc}$, H-6a$_{Glc}$, H-6b$_{Glc}$, H-2$_{Gal}$, H-3$_{Gal}$, H-4$_{Gal}$, H-5$_{Gal}$, H-6a$_{Gal}$, H-6b$_{Gal}$), 3.40 (m, 4 H, N(CH_2R)$_2$), 1.62 (m, 4 H, N(CH$_2$CH_2R)$_2$), 1.23 (m, 36 H, 18 CH_2), 0.98 (t, 6H, J 6.2 Hz, 2 CH_3). ^{13}C NMR (C_5D_5N): δ 159.25 (C-1'), 150.81 (C-4''), 148.69 (C-4'), 143.40 (C-1''), 125.44 (C-2'', C-6''), 123.95 (C-3', C-5'), 117.13 (C-2', C-6'), 111.69 (C-3'', C-5''), 105.40 (C-1$_{Gal}$), 101.31 (C-1$_{Glc}$), 80.92 (C-4$_{Glc}$), 77.03, 76.57, 76.20 (C-3$_{Gal}$, C-5$_{Gal}$ C-5$_{Glc}$), 74.79, 74.10 (C-2$_{Glc}$, C-3$_{Glc}$), 72.18 (C-2$_{Gal}$), 69.76 (C-

4_{Gal}), 61.83 (C-6_{Glc}), 61.18 (C-6_{Gal}) 51.12 (N(*C*H_2R)$_2$), 31.96, 29.73, 29.62, 29.44, 27.56, 27.10, 22.78 (*C*H_2 alkyl chains), 14.15 (2 *C*H_3). Anal. Calcd for $C_{48}H_{79}N_3O_{11}$,1.5H_2O (901.16): C, 63.97; H, 9.17; N, 4.66. Found; C, 63.97; H, 9.11; N, 4.70.

4-(4'-N,N-Didodecylaminophenylazo)phenyl β-D-xylopyranoside (**5d**)

Compound **5d** was obtained from **4d** in 95% as described above, after purification by column chromatography (EtOAc). Product **5d** was a red amorphous solid: R_f 0.50 (EtOAc); $[\alpha]_D$ 22.0 (*c* 0.25, $CHCl_3$). UV/vis: λ_{max} = 271 nm, ε = 154500; λ_{max} = 416 nm, ε = 21000. ^{1}H NMR (CD_3COCD_3): δ 7.79 (d, 4 H, *J* 7.9 Hz, H-3', H-5', H-2'', H-6''), 7.16 (d, 2 H, *J* 7.9 Hz, H-2', H-6'), 6.81 (d, 2 H, *J* 7.9 Hz, H-3'', H-5''), 5.05 (dd, 1 H, $J_{1,2}$ 5.1, $J_{1,3}$ 2.0 Hz, H-1), 4.38 (dd, 1 H, $J_{4,5a}$ 4.5, $J_{5a,5b}$ 10.8 Hz, H-5a), 3.63-3.40 (m, 8 H, H-2, H-3, H-4, H-5b, N(C*H*$_2$R)$_2$), 1.68 (m, 4 H, N(CH_2C*H*$_2$R)$_2$), 1.30 (m, 36 H, 18 C*H*$_2$), 0.89 (t, 6H, *J* 6.6 Hz, 2 C*H*$_3$). ^{13}C NMR ($CDCl_3$): δ 157.63 (C-1'), 150.26 (C-4''), 149.06 (C-4'), 143.07 (C-1''), 125.12 (C-2'', C-6''), 123.78 (C-3', C-5'), 117.07 (C-2', C-6'), 111.10 (C-3'', C-5''), 101.02 (C-1), 76.07 (C-4), 73.08 (C-3), 69.62 (C-2), 65.49 (C-5), 51.27 (N(*C*H_2R)$_2$), 31.99, 29.75, 29.56, 29.43, 27.45, 27.21, 22.76 (*C*H_2 alkyl chains), 14.20 (2 *C*H_3). Anal. Calcd for $C_{41}H_{67}N_3O_5$,0.5H_2O (690.975): C, 71.26; H, 9.77; N, 6.08. Found; C, 71.20; H, 9.85; N, 6.13.

4-(4'-N,N-Didodecylaminophenylazo)phenyl α-D-mannopyranoside (**5e**)

Compound **5e** was obtained from **4e** in 93% yield as described above, after purification by column chromatography (8:1 EtOAc-EtOH). Product **5e** was a red amorphous solid: R_f 0.68 (8:1 EtOAc-EtOH). $[\alpha]_D$ 55.6 (*c* 0.5, $CHCl_3$). UV/vis: λ_{max} = 271 nm, ε = 96000; λ_{max} = 416 nm, ε =

24000. ^{1}H NMR ($CDCl_3$): δ 7.78 (m, 4 H, *J* 8.9 Hz, H-3', H-5', H-2'', H-6''), 7.24 (d, 2 H, *J* 8.9 Hz, H-2', H-6'), 6.78 (d, 2 H, *J* 9.2 Hz, H-3'', H-5''), 5.62 (d, 1 H, $J_{1,2}$ 1.2 Hz, H-1), 4.08 (dd, 1 H, $J_{2,3}$ 3.1 Hz, H-2), 3.94 (dd, 1 H, $J_{3,4}$ 9.2 Hz, H-3), 3.85 (dd, 1 H, $J_{4,5}$ 9.2 Hz, H-4), 3.7-3.63 (m, 3 H, H-5, H-6a, H-6b), 3.45 (m, 4 H, N(CH_2R)$_2$), 1.67 (m, 4 H, N(CH$_2$CH_2R)$_2$), 1.30 (m, 36 H, 18 CH_2), 0.88 (t, 6H, *J* 6.6 Hz, 2 CH_3). ^{13}C NMR ($CDCl_3$): δ 157.10 (C-1'), 150.18 (C-4''), 148.60 (C-4'), 143.16 (C-1''), 125.03 (C-2'', C-6''), 123.76 (C-3', C-5'), 116.76 (C-2', C-6'), 111.12 (C-3'', C-5''), 98.43 (C-1), 73.48 (C-5), 71.65, 70.89 (C-2, C-3), 66.30 (C-4), 61.03 (C-6), 51.27 (N(*C*H$_2$R)$_2$), 32.00, 29.74, 29.60, 29.43, 27.47, 27.21, 22.76 (*C*H$_2$ alkyl chains), 14.19 (2 *C*H$_3$). Anal. Calcd for $C_{42}H_{69}N_3O_6$,0.5H_2O (721.00): C, 69.96; H, 9.78; N, 5.83. Found; C, 70.25; H, 9.86; N, 5.67.

2. Evaluation of Physical Properties

Phase identifications and determination of phase transition temperatures were carried out, concomitantly, by thermal polarized light microscopy using either a Zeiss Universal polarizing transmitted light microscope equipped with a Mettler FP52 microfurnace in conjunction with an FP50 Central Processor. Photomicrographs were obtained using a Zeiss polarizing light microscope equipped with a Nikon AFM camera. Homeotropic sample preparations suitable for phase characterization were prepared simply by using very clean glass microscope slides (washed with water, acetone, water, concentrated nitric acid, water and dry acetone). Homogenous specimens were obtained using untreated glass slides and cover slips. Differential scanning calorimetry was used to determine enthalpies of transition and to confirm the phase transition temperatures determined by optical microscopy. Differential scanning thermograms

(scan rate 10° min^{-1}) were obtained using a Perkin Elmer DSC 7 PC system operating on DOS software. The results obtained were standardized to indium (measured onset 156.68 °C, ΔH 28.47 J g^{-1}, lit. value 156.60 °C, ΔH 28.45 Jg^{-1})[41].

Comparison of the transition temperatures determined by optical microscopy and differential scanning calorimetry show some slight discrepancies, *ie,* up to about 3 °C in some cases. This is due to the carbohydrates which tended to decompose at elevated temperatures and at different rates depending on the rate of heating, the time spent at an elevated temperature and the nature of the supporting substrate, *i.e.*, the materials decomposed more quickly in aluminum DSC pans than on glass microscope slides. In addition, *cis-trans* isomerization of the materials, particularly in the light microscope, also led to changes in phase transition temperatures.

The X-ray diffraction experiments were performed on a MAR345 diffractometer equipped with a 2D image plate detector (CuKα radiation, graphite monochromator, λ = 1.54 Å). The samples were heated in the presence of a magnetic field (B ≈ 1T) using a home-built capillary furnace. The diffraction patterns show the intensity as a function of the modulus of the scattering wave vector (q);

$$q = |q|4\pi\sin\theta/\lambda = 2\pi n/d$$

where θ is the diffraction angle, λ is the wavelength (1.54 Å), n is an integer and d is the lattice distance. Although a magnetic field was applied upon heating, little or no alignment of the samples was achieved.

Molecular lengths were determined either by using Dreiding molecular models or *via* computer simulations using an Apple MacIntosh G4 computer and *ChemDraw3D*^{TM} as part of a *ChemDraw Ultra 6.0* program.